

Hybrid bioinorganic approach to solar-to-chemical conversion

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Natural photosynthesis harnesses solar energy to convert CO₂ and water to value-added chemical products for sustaining life. We present a hybrid bioinorganic approach to solar-to-chemical conversion in which sustainable electrical and/or solar input drives production of hydrogen from water splitting using biocompatible inorganic catalysts. The hydrogen is then used by living cells as a source of reducing equivalents for conversion of CO₂ to the value-added chemical product methane. Using platinum or an earth-abundant substitute, α -NiS, as biocompatible hydrogen evolution reaction (HER) electrocatalysts and *Methanosarcina barkeri* as a biocatalyst for CO₂ fixation, we demonstrate robust and efficient electrochemical CO₂ to CH₄ conversion at up to 86% overall Faradaic efficiency for ≥ 7 d. Introduction of indium phosphide photocathodes and titanium dioxide photoanodes affords a fully solar-driven system for methane generation from water and CO₂, establishing that compatible inorganic and biological components can synergistically couple light-harvesting and catalytic functions for solar-to-chemical conversion.

artificial photosynthesis | solar fuels | photocatalysis | carbon dioxide fixation | water splitting

Methods for the sustainable conversion of carbon dioxide to value-added chemical products are of technological and societal importance (1–3). Elegant advances in traditional approaches to CO₂ reduction driven by electrical and/or solar inputs using homogeneous (4–16), heterogeneous (17–26), and biological (7, 27–31) catalysts point out key challenges in this area, namely (i) the chemoselective conversion of CO₂ to a single product while minimizing the competitive reduction of protons to hydrogen, (ii) long-term stability under environmentally friendly aqueous conditions, and (iii) unassisted light-driven CO₂ reduction that does not require external electrical bias and/or sacrificial chemical quenchers. Indeed, synthetic homogeneous and heterogeneous CO₂ catalysts are often limited by product selectivity and/or aqueous compatibility, whereas enzymes show exquisite specificity but are generally less robust outside of their protective cellular environment. In addition, the conversion of electrosynthetic systems to photosynthetic ones is nontrivial owing to the complexities of effectively integrating components of light capture with bond-making and bond-breaking chemistry.

Inspired by the process of natural photosynthesis in which light-harvesting, charge-transfer, and catalytic functions are integrated to achieve solar-driven CO₂ fixation (32–35), we have initiated a program in solar-to-chemical conversion to harness the strengths inherent to both inorganic materials chemistry and biology (36). As shown in Fig. 1, our strategy to drive synthesis with sustainable electrical and/or solar energy input (37) interfaces a biocompatible photo(electro)chemical hydrogen evolution reaction (HER) catalyst with a microorganism that uses this sustainably generated hydrogen as an electron donor for CO₂ reduction. Important previous reports have shown the feasibility of electrosynthesis (38–42) but have not yet established solar-driven processes. We selected methane as an initial target for this approach owing to the ease of product separation, the potential for integration into

existing infrastructures for the delivery and use of natural gas (of which CH₄ is the principle component), and the fact that direct conversion of CO₂ to CH₄ with synthetic catalysts remains a formidable challenge due to large overpotentials and poor CH₄/H₂ selectivity. Two of the most active and selective direct electrocatalysts for CO₂ to CH₄ conversion reported to date produce methane with 61% (43) and 76% (44) Faradaic efficiencies, but require overpotentials of $\eta = 1.28$ V and $\eta = 1.52$ V, respectively. Promising advances in photothermal reduction of CO₂ to CH₄ also have been recently reported (45). In comparison with fully inorganic catalysts, a distinct conceptual advantage of this hybrid materials biology approach, where the materials component performs water splitting to generate hydrogen and the biological component uses these reducing equivalents for CO₂ fixation, is that one can leverage the fact that biological catalysts operate at near thermodynamic potential (46). As such, the only overpotential involved is associated with hydrogen evolution from water, a more facile reaction to catalyze via sustainable electrochemical and photochemical means compared with CO₂ reduction. Coupled with the diversity of potential chemical products available via synthetic biology, the marriage between artificial and natural platforms can create opportunities to develop catalyst systems with enhanced function over the individual parts in isolation.

In developing hybrid bioinorganic platforms for solar-to-chemical conversion of CO₂, we drew inspiration from both

Significance

Natural photosynthesis, a process of solar-to-chemical conversion, uses light, water, and carbon dioxide to generate the chemical products needed to sustain life. Here we report a strategy inspired by photosynthesis in which compatible inorganic and biological components are used to transform light, water, and carbon dioxide to the value-added product methane. Specifically, this solar-to-chemical conversion platform interfaces photoactive inorganic materials that produce hydrogen from water and sunlight with microorganisms that consume this sustainably derived hydrogen to drive the transformation of carbon dioxide to methane with high efficiency. This system establishes a starting point for a broader materials biology approach to the synthesis of more complex chemical products from carbon dioxide and water.

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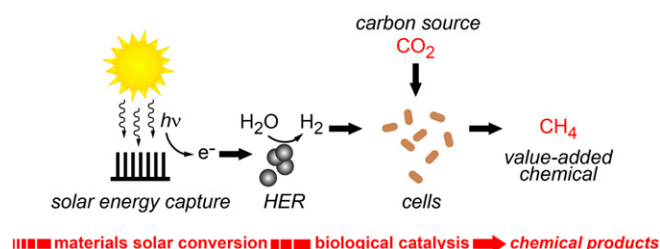


Fig. 1. General scheme depicting a hybrid bioinorganic approach to solar-to-chemical conversion. Sustainable energy inputs in the form of electrical potential or light can be used to generate hydrogen from water using inorganic HER catalysts; biological hydrogen-driven CO_2 fixation can subsequently generate value-added products such as methane. This materials biology interface can be generalized to other chemical intermediates and end products by mixing and matching different compatible inorganic and biological components.

tandem organometallic–microbial systems (47, 48), in which products of microbial metabolism are further transformed by organometallic catalysts, as well as biological electrosynthesis, in which organisms accept reducing equivalents from an electrode either in the form of soluble electron carriers (for example, H_2 or formate) (41, 49, 50) or via direct electron transfer (36, 51–53). Engineered strains of *Ralstonia eutropha* have been used for the aerobic production of isobutanol and 3-methyl-1-butanol (41), and isopropanol (42). However, owing to the oxygen requirements of this organism and the relative inefficiency of its carbon fixation pathways (54), product titers and production efficiencies are relatively modest, and generation of reactive oxygen species is a serious concern. In addition, to our knowledge, no photosynthetic systems of this type have been reported. As such, we turned our attention to the use of a pure culture of *Methanosarcina barkeri*, an obligately anaerobic archaeon that fuels its metabolism via the 8-proton, 8-electron reduction of CO_2 to CH_4 (55). Prior studies have reported methanogenic electrosynthesis (51, 53, 56); however, a fully light-driven system remains to be realized. Additionally, mixed cultures and multiple possible sources of reducing equivalents have complicated Faradaic efficiency measurements in previous studies (51, 53, 56). Through the design of our hybrid system, we sought to surmount some of these aforementioned challenges.

Here we report an integrated bioinorganic catalyst platform for solar-to-chemical CO_2 conversion using sustainable inorganic hydrogen generators in conjunction with CO_2 -fixing archaea. Under electrosynthetic conditions with a platinum cathode, a culture of *M. barkeri* shows chemoselective conversion of CO_2 to CH_4 with high Faradaic efficiencies (up to 86%) and low overpotential ($\eta = 360$ mV). The system is also capable of high yield production, cumulatively generating 110 mL (4.3 mmol) of methane over 7 d. Isotope labeling with $^{13}\text{CO}_2$ establishes that CH_4 is uniquely derived from CO_2 for cultures in both rich media and minimal, carbon-free media. Replacement of Pt with an earth-abundant α -NiS electrocatalyst allows for CH_4 generation at similar titers. Moreover, using a photoactive silicon cathode reduces the overpotential to 175 mV upon irradiation with 740-nm light. Unassisted light-driven methane generation was achieved using tandem solar absorption by a photoactive *n*- TiO_2 anode and *p*-InP cathode assembly. Taken together, the results demonstrate the feasibility of combining compatible inorganic and biological systems to achieve solar-to-chemical conversion from light, H_2O , and CO_2 , affording a starting point for the realization of sustainable fixation of CO_2 to value-added molecules.

Results and Discussion

Selection of Biological Catalyst. Careful organism selection is critical to the successful realization of an integrated bioinorganic system. The autotrophic obligate anaerobe *M. barkeri* (55) is amenable to integration with inorganic catalysts for a variety of

reasons. *M. barkeri* can use H_2 as a source of reducing equivalents for the reduction of CO_2 to CH_4 ; the cathode of a water-splitting device could serve as a potential source of this H_2 . Owing to the anaerobic metabolism of the organism, oxygen is not required at the cathode, thereby improving Faradaic efficiency for the product of interest, simplifying gas delivery to the culture, and preventing generation of potentially harmful reactive oxygen species. Furthermore, CH_4 is generated with high efficiency as a byproduct of normal metabolism. Finally, *M. barkeri* requires no added sources of reduced carbon and can produce CH_4 in minimal media containing only supplemental vitamins and minerals.

Electrochemical Reduction of Carbon Dioxide to Methane with a Hybrid Platinum/Archaea Catalyst Platform. Initial experiments were performed using a platinum cathode to electrochemically generate H_2 , which was subsequently used in situ by *M. barkeri* to reduce CO_2 to CH_4 . Fig. 2A shows a general schematic of the gas-tight, two-compartment electrochemical cell that was specially fabricated for batch-mode electrolysis and subsequent headspace analysis by gas chromatography (GC). (See Fig. S1 for electrolysis cell photo.) Separation of the cathodic and anodic chambers with an ion-permeable membrane prevented any noticeable diffusion of O_2 into the culture. After inoculation of the cathodic chamber with *M. barkeri* (130-mL final volume, $\text{OD}_{600\text{ nm}} = 0.35$) and saturation of the carbon-free catholyte with pure CO_2 ,

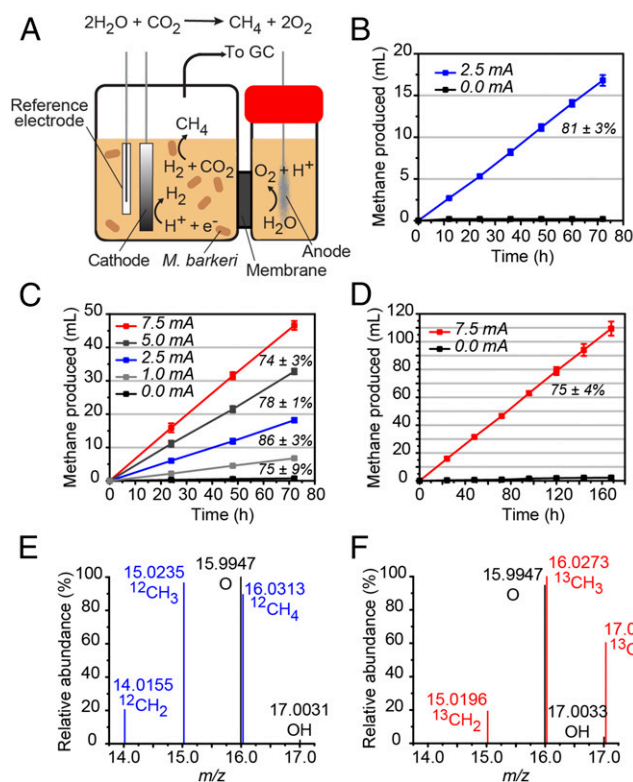


Fig. 2. Electrocatalytic reduction of carbon dioxide to methane with a hybrid platinum/*M. barkeri* platform. (A) Schematic of generalized electrolytic setup showing in situ generation of hydrogen at the cathode followed by hydrogen-driven reduction of carbon dioxide to methane by the *M. barkeri* biocatalyst. (B) Cumulative methane generation and associated average Faradaic efficiency in minimal media. (C) Cumulative methane generation and associated average Faradaic efficiencies at various currents in rich media. (D) Cumulative long-term methane generation and associated average Faradaic efficiency in rich media. (E and F) High-resolution mass spectrometry of headspace gases after electrolysis under an atmosphere of (E) $^{12}\text{CO}_2$ and (F) $^{13}\text{CO}_2$ in rich media. Error bars represent SD with $n = 3$ independent experiments in all cases.

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